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A novel hydrogen peroxide sensor based on Ag nanoparticles decorated polyaniline/graphene composites

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ABSTRACT: A novel electrochemical sensor based on Ag nanoparticles (AgNPs) decorated polyaniline/graphene composites (PANI/G) is developed, which can be used for sensitive determination of H_2O_2. For the construction of the H_2O_2 sensor, polyaniline (PANI) is first electrodeposited on the surface of graphene (G) to form PANI/G, and then horseradish peroxidase (HRP) loaded on AgNPs (HRP/AgNPs) is immobilized on to the PANI/G. H_2O_2 can be catalyzed by HRP to generate current response which can be significantly enhanced by AgNPs, and thus the PANI/G based sensor can be utilized for the detection of H_2O_2. Under the optimized conditions, the proposed H_2O_2 sensor exhibits wide linear response to H_2O_2 concentration ranging from 0.25 to 2.25 m*M* with a detection limit of 0.03 m*M* (signal-to-noise ratio of 3), and it also shows high selectivity and reproducibility. The method is simple and cost-effective, and can be a promising candidate as the sensitive sensing platform for H_2O_2. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42409.

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INTRODUCTION

Hydrogen peroxide (H_2O_2) is a kind of compounds called reactive oxygen species,[1] which is believed to be of great importance in the field of chemistry, biochemistry, and life sciences. Therefore, the simple, accurate and reliable measurement of H_2O_2 has become an attractive challenge for researchers in analytical chemistry. Currently, the determination of H_2O_2 is achieved via different techniques, such as chemiluminescence,[2] fluorimetry,[3,4] spectrophotometry,[5] and electrochemistry.[6] In comparison, electrochemical methods are advantageous due to simplicity, low-cost, celerity, high sensitivity, and selectivity.[7]

Enzymes (or proteins) are important biorecognition elements for electrochemical approach. Therefore, enzyme immobilization plays a key role in enzyme sensors for electrochemistry in view of heterogeneous direct electron transfer between electrode surfaces and redox enzymes. Moreover, one of the main challenges is to select a host matrix to provide a suitable microenvironment for the enzymes. Various electrochemical biosensors for H_2O_2 detection have been widely investigated using different materials for enzymes immobilization such as immobilization of cytochrome *c* on natural nano-attapulgite,[8] HRP on poly(*N*-[3-(trimethoxysilyl)-propyl]aniline) gold nanorods film,[9] catalase in nickel oxide nanoscale islands,[10] and myoglobin in zirconia nanoparticles enhanced grafted collagen hybrid composite.[11] Yamamoto *et al.*[12] reported an amperometric sensor for H_2O_2 detection utilizing multi-wall carbon nanotubes and HRP modified glassy carbon electrode, and it exhibited low working potential (−0.3 V), low detection limit (0.1 μM, $S/N = 3$) and a wide linear range from 0.3 μM to 0.2 m*M* in a continuous-flow cell containing H_2O_2. Zhang *et al.*[13] developed a H_2O_2 sensor by direct immobilization of HRP on zinc oxide nanorods grown on the electrode, and the biosensor responded well to H_2O_2 in a concentration range from 0.5 to 9 m*M* with a detection limit of 0.3 m*M* ($S/N = 3$) and a short response time of about 7 s. Wang *et al.*[14] prepared carbon nanodots and CoFe layered double hydroxide composites for immobilizing HRP to the glassy carbon electrode, and this proposed biosensor displayed good electrocatalytic reduction activity and excellent analytical performance toward H_2O_2. Up to date, the development and

application of H_2O_2 sensors is still restricted to some extent due to the lack of simple and stable immobilization approach and long-term stability of the immobilized enzymes.[15]

Graphene (G), a kind of carbon-based material, has attracted enormous interests in many applications due to its excellent mechanical strength, fast electron transferring rate, extraordinary electrical properties, and large specific surface area.[16–18] G is expected to be a perfect alternative electrode material instead of carbon nanotubes, with respect to the convenient and low-cost fabrication procedure. However, many of the unique and interesting properties of G can only be realized after it is integrated into more complex assemblies.[19] Zhou *et al.*[20] have constructed a novel H_2O_2 biosensor based on Au-G-HRP-chitosan biocomposites, and Shan *et al.*[21] have reported a glucose biosensor based on the combination of polyvinylpyrrolidone (PVP)-protected G and polyethylenimine functional ionic liquid. Li *et al.*[22] have immobilized HRP on the graphene modified electrode for the detection of H_2O_2. All the biosensors have achieved the direct electron transfer of the enzymes, while retaining the bioactivity of the enzymes and exhibiting excellent electrocatalysis performance.

In this work, we successfully utilized Ag nanoparticles (AgNPs) decorated polyaniline/graphene composites (PANI/G) to construct a novel H_2O_2 biosensor. AgNPs have been widely used in modification of various electrodes and fabrication of different kinds of biosensors, due to its large surface area, biocompatibility, and excellent electrical conductivity.[23] It has been reported that the integration of carbon-based materials and metal nanoparticles, such as G-AuNPs composites offers synergistic effect in electrocatalytic applications, so we also expect the G-AgNPs composite has the same effect. PANI, one of the most attractive conducting polymers, can act as an ideal matrix for enzyme electrodes to improve electrochemical signals in biosensor applications.[9] The as-prepared H_2O_2 biosensor based on the HRP/AgNPs/PANI/G composite shows excellent analytical performances, such as high sensitivity, enhanced stability, good selectivity, and short response time, and displays good electrocatalytic response for H_2O_2.

EXPERIMENTAL

Materials and Reagents

Aniline and HRP were purchased from Aladdin Chemicals Reagent (Shanghai, China). Aniline was distilled under reduced pressure before use. Natural flake graphite (99%, grain size 50 mesh) was obtained from Haida Graphite (Qingdao, China). Phosphate buffer solutions (PBS, 0.1*M*) with different pH values were prepared by mixing stock standard solutions of Na_2HPO_4 and NaH_2PO_4, and adjusting the pH with 0.1*M* NaOH or H_3PO_4. H_2O_2 (30 wt % aqueous) was purchased from Sinopharm Chemical Reagent (Shanghai, China). Other chemicals were of analytical reagent grade. Doubly distilled water was used in all of the experiments.

Apparatus and Methods

Electrochemical measurements were carried out on a CHI660D electrochemical workstation (Chenhua Instruments, Shanghai, China) with a conventional three-electrode system comprised of platinum foil as counter electrode, saturated calomel electrode (SCE) as reference electrode and HRP/AgNPs/PANI/G modified glassy carbon electrode (GCE) as working electrode. The amperometric measurements in response to H_2O_2 were performed at an applied potential of +0.8 V in 0.1*M* PBS of pH 7.0 under stirring at room temperature. The electrolyte was deoxygenated by purging pure nitrogen for 20 min prior to the experiments, and the solutions were kept under a nitrogen atmosphere during the electrochemical experiments.

Preparation of AgNPs

AgNPs were prepared according to the previous literature[24] with slight modification. 0.65 g of PVP and 40 mL of anhydrous ethanol were mixed and then refluxed at 70°C. 0.20 g of $AgNO_3$ was added to the resulting solution, and the mixture was refluxed at 70°C until the color was changed. Then the mixture was cooled down to room temperature and stored until use. All the glasswares used in this process were washed with freshly prepared 1 : 3 (v/v) HNO_3/HCl and doubly distilled water several times.

Preparation of H_2O_2 Sensor

A GCE (3 mm diameter) was polished carefully to a mirror-like surface with fine emery papers and 0.3 and 0.05 μm alumina slurry, sonicated in water, and ethanol for 10 min, respectively, and then allowed to dry at room temperature. Graphene oxide (GO) was synthesized from natural graphite powder according to an improved Hummers' method.[25] 10 μL of GO dispersion (1 mg/mL) was dropped onto the surface of the GCE, and then allowed to dry in air. The GO/GCE was reduced at −1.0 V for 90 min in 0.1*M* PBS to form G modified GCE (G/GCE).[26,27]

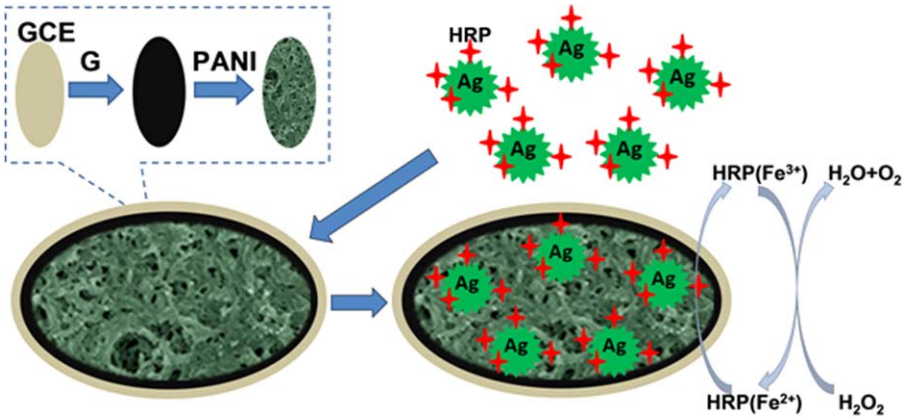
The electrosynthesis of PANI on the G/GCE was carried out in 0.1 M H_2SO_4 solution containing 10 m*M* aniline using repeated potential cycling. The sweeping potential range was set between −0.2 V and 1.1 V at a scan rate of 100 mV/s. The electrolysis was finished after 10 cycles, and then the obtained PANI modified G/GCE (PANI/G/GCE) was rinsed with doubly distilled water and dried at room temperature.

10 μL dispersion solution containing 10 mg/mL HRP and 3 mg/mL AgNPs was cast on to the surface of the PANI/G/GCE and dried at room temperature. The resulting HRP/AgNPs/PANI/G/GCE was rinsed with 0.1*M* PBS (pH 7.0) several times to remove loosely adsorbed HRP/AgNPs, and then 5 μL of nafion (5 wt %) was cast on to the electrode surface to maintain the stability of the sensor. When not in use, the as-prepared H_2O_2 sensor was stored in 0.1*M* PBS (pH 7.0) in a refrigerator at 4°C. The preparation process of the modified electrode is shown in Scheme 1.

RESULTS AND DISCUSSION

Electrochemical Characterization of PANI/G Modified GCE

PANI can be a good matrix for enzyme immobilization, however, the conductivity of PANI is not satisfactory ($\sim 1.0 \times 10^{-8}$ S/cm),[6] so the concentration of aniline will influence the electron transfer ability at the PANI/G-solution interface. Figure 1(A) shows the cyclic voltammograms (CVs) of PANI/G obtained from different concentrations of aniline (0, 5, 10, 20, and 50 m*M*). A pair of redox peaks due to the oxidation and



Scheme 1. Preparation process for HRP/AgNPs/PANI/G/GCE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

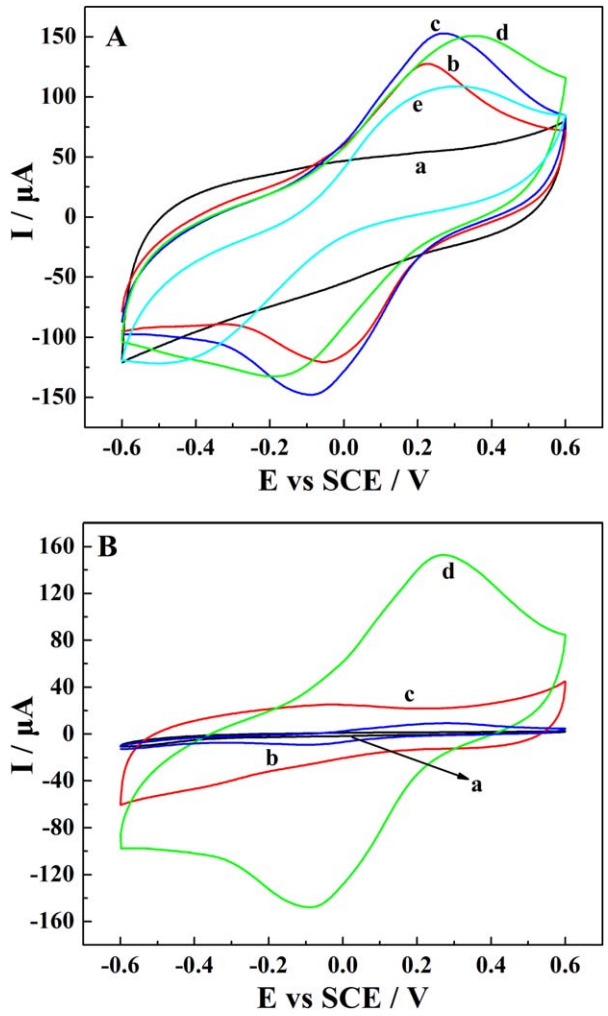


Figure 1. Cyclic voltammograms of (A) PANI/G modified GCE prepared from (a) 0, (b) 5, (c) 10, (d) 20, and (e) 50 m*M* aniline and (B) modified electrodes (a) GO/GCE, (b) PANI/GO/GCE, (c) G/GCE, and (d) PANI/G/GCE in N_2-saturated 0.1*M* PBS (pH 7.0). Scan rate: 100 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reduction of PANI appeared at 0.23 and −0.09 V, respectively, when the concentration of aniline monomer was 5 m*M*, indicating that the polymerization of aniline can occur at a concentration as low as 5 m*M*. This phenomenon is attributed to the catalytic effect of G for the synthesis of PANI,[28] because the delocalized π-electron system of G can form a strong π-stacking interaction with aromatic compounds.[29–31] The peak current increased a lot when the concentration of aniline increased to 10 m*M*, since the PANI film obtained at 10 m*M* is thicker than that at 5 m*M*. However, when the concentration of aniline increased further to 20 or 50 m*M*, the prepared PANI film exhibited lower electroactivity compared to that obtained from 10 m*M*, this is because that a too thick PANI film will hinder the electron transfer at the electrode–solution interface, resulting in a decrease in the redox peak currents.

Figure 1(B) shows the CVs of GO, G, PANI/GO, and PANI/G modified GCE in N_2-saturated 0.1*M* PBS. As can be seen, no redox peaks can be observed at both GO and G modified GCE, indicating that G and GO are electroinactive in the wide potential window. A pair of well-defined redox peaks is found at the PANI/G and PANI/GO modified GCE with an anodic peak at 0.25 V and a cathodic peak at −0.09 V, which is caused by the electrochemical oxidation and reduction of PANI. And it is noteworthy that the peak currents at the PANI/G/GCE are remarkably higher than those at the PANI/GO/GCE. The reason can be attributed to the fact that G has excellent conductivity (curves a and c) compared with GO, and thus it can facilitate the electron transfer at the electrode–solution interface, accompanied with the significant increase in the redox peak currents.

Electrocatalysis of HRP/AgNPs/PANI/G/GCE to the Reduction of H_2O_2

Electrochemical behaviors of H_2O_2 at different modified electrodes were also investigated. Figure 2 shows the CVs of different modified electrodes in the presence and absence of H_2O_2 in N_2-saturated 0.1*M* PBS. Compared with the systems without H_2O_2 (curves a and b), the cathodic peak currents increase dramatically when 25 m*M* H_2O_2 was added to the buffer solution (curves c and d), indicating that the HRP/PANI/G/GCE and HRP/AgNPs/PANI/G/GCE have excellent catalytic activity toward H_2O_2. The mechanism of HRP catalysis reaction toward

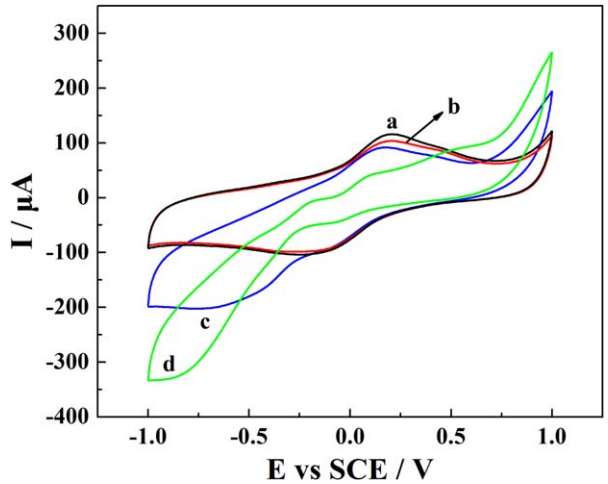


Figure 2. Cyclic voltammograms of (a) HRP/AgNPs/PANI/G/GCE and (b) HRP/PANI/G/GCE in N_2-saturated 0.1*M* PBS without H_2O_2, and (c) HRP/PANI/G/GCE and (d) HRP/AgNPs/PANI/G/GCE in N_2-saturated 0.1*M* PBS containing 25 m*M* H_2O_2. Scan rate: 100 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

H_2O_2 has been well described previously,[32,33] as shown in Scheme 1. Here, it is noteworthy that the cathodic peak current at the HRP/AgNPs/PANI/G/GCE is enhanced significantly compared with that at the HRP/PANI/G/GCE, demonstrating that AgNPs play a key role in signal amplification. The amplification of cathodic peak current by AgNPs can be explained as followed. AgNPs have large specific surface area and can combine well with the enzyme molecules, resulting in interactions between AgNPs and enzyme molecules.[32] In addition, AgNPs have a good biocompatibility and can make the enzyme molecules retaining good biological activity. When AgNPs are used for electrodes decoration, they can shorten the distance between the HRP center and the electronic tunnel on the electrode surface, and thus faciliate the electron transfer between the electrode and the enzyme.[34,35]

Effect of applied potential on amperometric responses of the HRP/AgNPs/PANI/G/GCE in the presence of 2 m*M* H_2O_2 was investigated in the range from 0.5 to 0.9 V [Figure 3(A)]. As can be seen, the steady-state current increases rapidly with the increase in the applied potential from 0.5 to 0.9 V. However, the enzyme electrode generates unneglectable background noise when the applied potential reaches as high as 0.9 V. Considering the sensitivity and low-noise background, 0.8 V is selected as the applied potential in the subsequent experiments. The relationship between current and pH and temperature in the presence of 2 m*M* H_2O_2 are shown in Figure 3(B). It shows that the response current increases from pH 5.0 to 7.0 and then decreases at higher pH values, and this is probably due to the fact that strongly acidic or alkaline environments would result in the denaturation of enzyme [black curve in Figure 3(B)]. Therefore, the maximum response is obtained at pH 7.0, which agrees well with previous reports.[36,37] As shown in Figure 3(B) (red curve), the variation tendency in current versus temperature is almost the same as that in current versus pH. This is

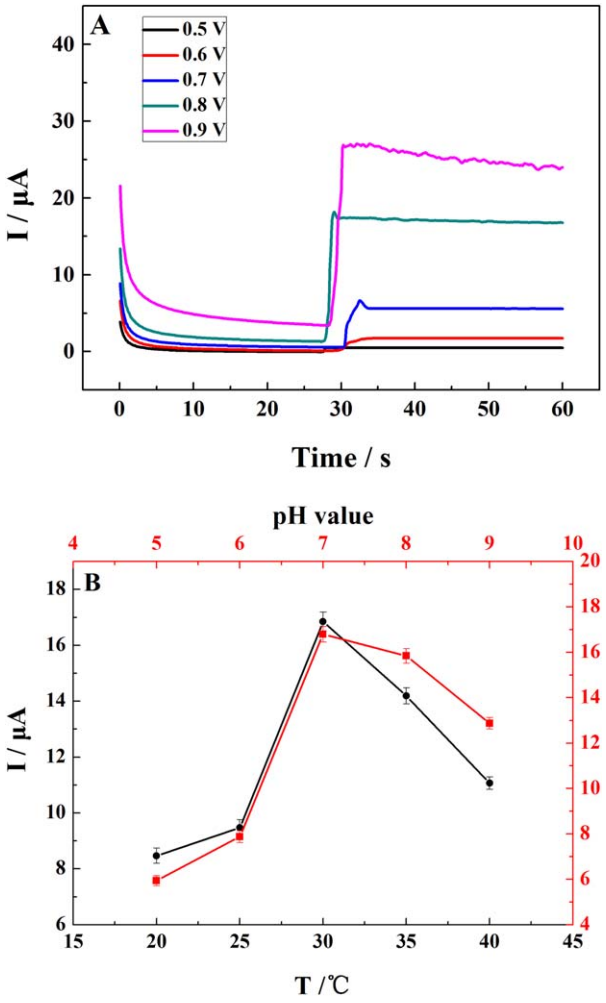


Figure 3. Effect of (A) applied potential, (B) pH and temperature on the amperometric responses of HRP/AgNPs/PANI/G/GCE in N_2-saturated 0.1*M* PBS containing 2 m*M* H_2O_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

because that high temperature will lead to partial inactivation of the immobilized HRP molecules, and further deteriorate the catalytic activity of the enzyme, resulting in the decline of the response current. And therefore, the subsequent experimental temperature is selected at 30°C.

Figure 4(A) shows the typical chronoamperometric response of the modified electrode upon successive addition of 0.25 m*M* H_2O_2 into a continuous stirring N_2-saturated PBS (0.1*M*, pH = 7) at an applied potential of 0.8 V. The current response achieves more than 98% of the steady-state current within 3 s, indicating a fast amperometric response to H_2O_2. The sensor displays a linear response to H_2O_2 in the concentration range between 0.25 and 2.25 m*M* with a correlation coefficient of 0.9978 [inset of Figure 4(A)], and the detection limit is estimated to be 0.03 m*M* at a signal-to-noise of 3 with a relatively high sensitivity of 7.46 μA/m*M*. The apparent Michaelis–Menten constant (K_M) is an indicator reflecting the kinetics of the enzyme–substrate reaction, and is calculated to be 5.03 m*M* from the slope and the intercept of the plot of the reciprocals of the steady-state current versus H_2O_2 concentration

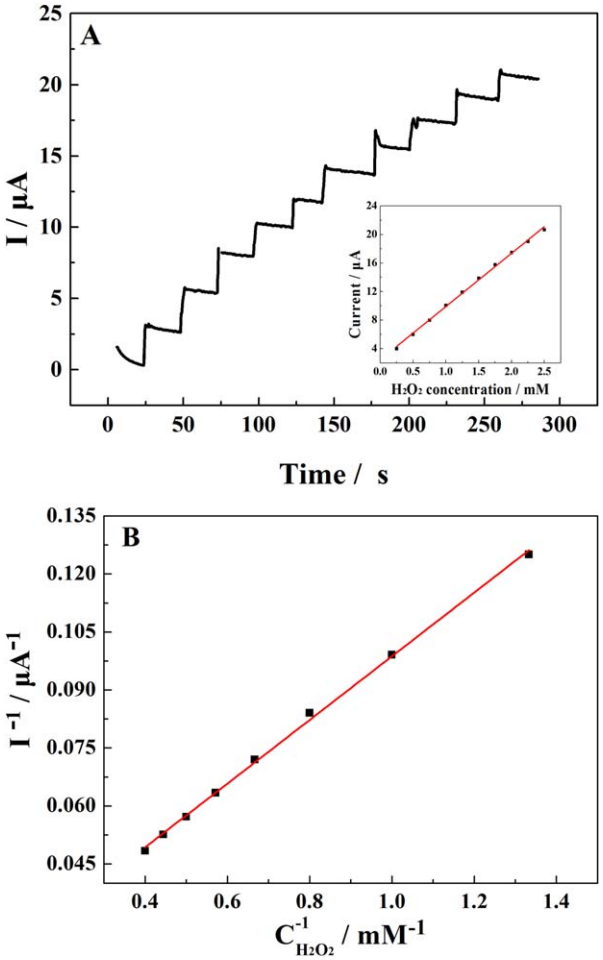


Figure 4. (A) Typical chronoamperometric response of the modified electrode upon successive additions of H_2O_2 at applied potential of 0.8 V. Inset: the calibration curve of current versus H_2O_2 concentration. (B) Lineweaver–Burk plot of current − 1 versus CH_2O_2 − 1 based on the data from the inset of (A). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[Figure 4(B)] based on the Lineweaver–Burk equation. It is well known that the smaller K_M indicates higher catalytic activity of the enzyme electrode,[38,39] and the low K_M value in this work indicates that the modified electrode exhibits a high enzymatic affinity.

Interference Study

Since enzyme–substrate reaction has its specificity, the specificity of the H_2O_2 sensor was also investigated. Here, glucose and ascorbic acid (AA) were chosen as the interferents. Figure 5 shows the amperometric response after adding 2 m*M* H_2O_2, 2 m*M* glucose and 2 m*M* AA into 20 mL 0.1*M* N_2-saturated PBS under continuous stirring. As shown, the H_2O_2 sensor exhibits excellent specificity to H_2O_2, demonstrating that these interferents coexisting in the sample matrix do not affect the determination of H_2O_2 with the as-prepared modified electrode.

Reproducibility and Stability of the H_2O_2 Sensor

The reproducibility of the as-prepared H_2O_2 sensor was estimated by successive determining 0.25 m*M* H_2O_2 with the same

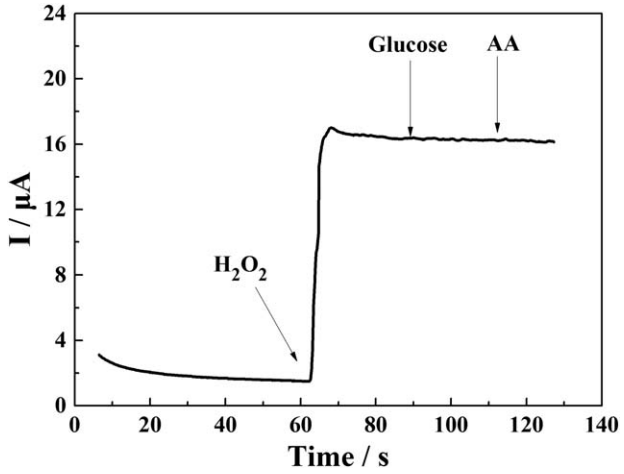


Figure 5. Amperometric response of the modified electrode to H_2O_2, glucose, and AA at an applied potential of 0.8 V in N_2-saturated 0.1*M* PBS (pH 7.0).

modified electrode, and the relative standard deviation (RSD) was 3.7% for five successive assays, indicating that the H_2O_2 sensor has a satisfactory determination precision. The stability of the sensor was also evaluated by measuring the current response of 2 m*M* H_2O_2. When the sensor was stored in 0.1*M* PBS (pH 7.0) at 4°C and measured after 1 week, the response remained at 94% of the initial response. This result indicates that HRP can retain its bioactivity within the modified electrode for a long period of time. The good reproducibility and stability of the sensor might be due to the fact that HRP molecules were firmly immobilized in the electrode by the proposed approach.

CONCLUSIONS

In this work, HRP is combined with AgNPs, PANI, and G to construct a novel H_2O_2 sensor. The as-prepared sensor realizes the direct electron transfer between HRP and the electrode and exhibits the typical electrocatalysis for H_2O_2. The PANI works as a host matrix and the AgNPs can greatly improve the sensitivity of the sensor. In addition, the H_2O_2 sensor exhibits satisfactory characteristics such as broad linear detection range, low detection limit, quick response time, acceptable reproducibility, and high sensitivity and stability. In summary, it can be a good alternative method for the construction of H_2O_2 sensors on the direct electrochemistry and can be applied in the immobilization of other bioactive molecules.

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